AB INITIO MODELING OF THERMOMECHANICAL PROPERTIES OF Mo-BASED ALLOYS FOR FOSSIL ENERGY CONVERSION

NETL Project DE-FE0004007

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University Coal Research Contractors Review Conference
Pittsburgh, PA May 30-31, 2012

Outline

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c. Revised phonon calculation for 5 crystals

IV. Conclusions on the work for Year 2

V. Plan for the next year

VI. Reviews of milestone goals

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I. Background

♠ The main objective of this project is to carry out extensive computational modeling on Mo-based alloys that can be used in a high temperature and high pressure environment.

♠ Specific aims are:

1. To develop new methods for calculating thermomechanical properties at extreme conditions.

2. To explore material properties within the Mo-Si-B system using a supercell approach.

3. To understand the enhanced properties at the fundamental level.

4. To establish effective collaborations with other research groups.

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II. Accomplishments in Year 1
(reported at the last review meeting)

- ♠ Electronic structure and interatomic bonding calculations in 5 crystals within the Mo-Si-B system: $MoSi_2$, Mo_3Si, Mo_2B, Mo_5Si_3 and Mo_5SiB_2.
- ♠ Mechanical properties of the same 5 crystals.
- ♠ <u>Preliminary</u> calculations on the phonon spectra of the these crystals.
- ♠ Computational development for uniaxial tensile experiments.

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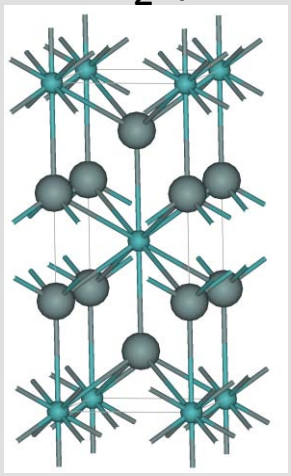
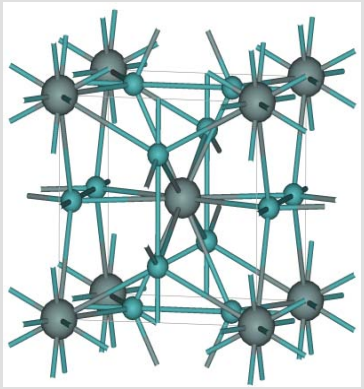
The following 5 crystals were studied in detail

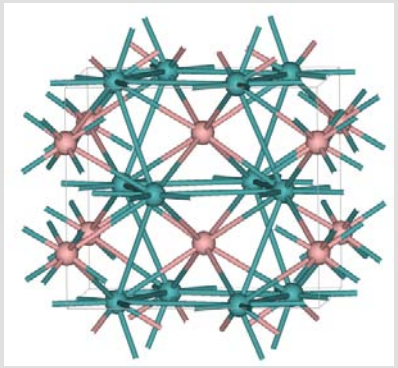
$MoSi_2$ (b.c.t)



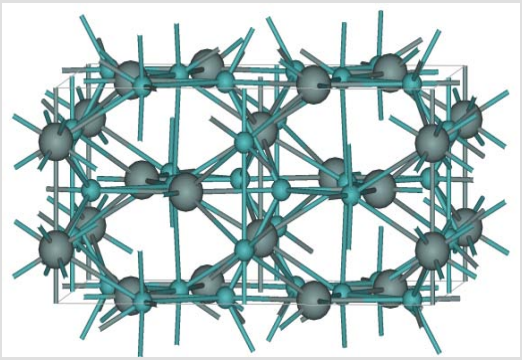
Mo_3Si (b.c.c)



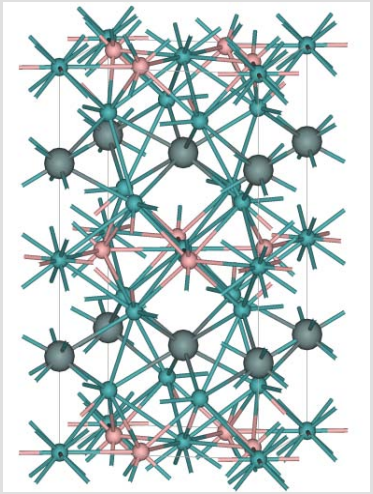
Mo_2B (b.c.t)

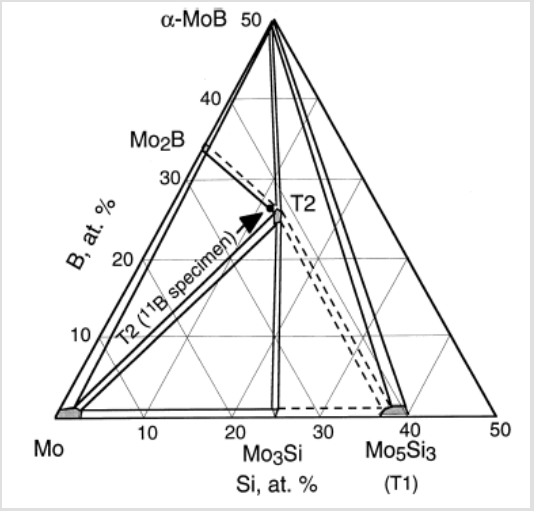


Mo_5Si_3 (b.c.t)



Mo_5SiB_2 (b.c.t)





Portion of the Mo-Si-B phases diagram.

Technical approach and methods used

Methods:

♠ **OLCAO** (Orthogonalized linear combination of atomic orbitals) developed by us. Used for electronic structure, bonding, optical properties, XANES/ELNES calculations.

♠ **VASP** (Vienna *Ab initio* Simulation Package): Used for structural relaxation, mechanical properties and tensile experiments on supercomputers.
A strain (ε_i) vs. stress (σ_i) analysis approach is used to obtain elastic constants C_{ij}. From the C_{ij}, the bulk modulus (K), shear modulus (G), Young's modulus (E), and Poisson's ratio (η) are evaluated using the Voigt-Reuss-Hill (VRH) approximation.

♠ ***Ab initio* phonon and thermodynamic calculations***. This is done within the quasi harmonic approximation (QHA) valid for temperatures < 1800K-2000K. The computational effort for *ab initio* phonon calculations is extremely demanding and require extensive code development and modification.

* Based on the *G(p,t)* package developed by Lizhi Ouyang (TSU)

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More on the OLCAO method

OLCAO (orthogonalized linear combination of atomic orbitals)

A. Use LDA approximation.

B. Basis expanded in term of atomic orbitals consisting of Gaussians: minimal basis (MB), full basis (FB), or extended basis (EB) for different purposes.

C. Economic basis expansion is the key to large complex systems.

1) Effective charge on each atom α: (for charge transfer)

$$Q_\alpha^* = \sum_i \sum_{n,occ} \sum_{j,\beta} C^{*n}_{i\alpha} C^n_{j\beta} S_{i\alpha,j\beta}$$

2) Bond order between atoms α and β: (for bond strength)

$$\rho_{\alpha\beta} = \sum_{n,occ} \sum_{i,j} C^{*n}_{i\alpha} C^n_{j\beta} S_{i\alpha,j\beta}$$

3) Site-and orbital decomposed partial density of states (PDOS).

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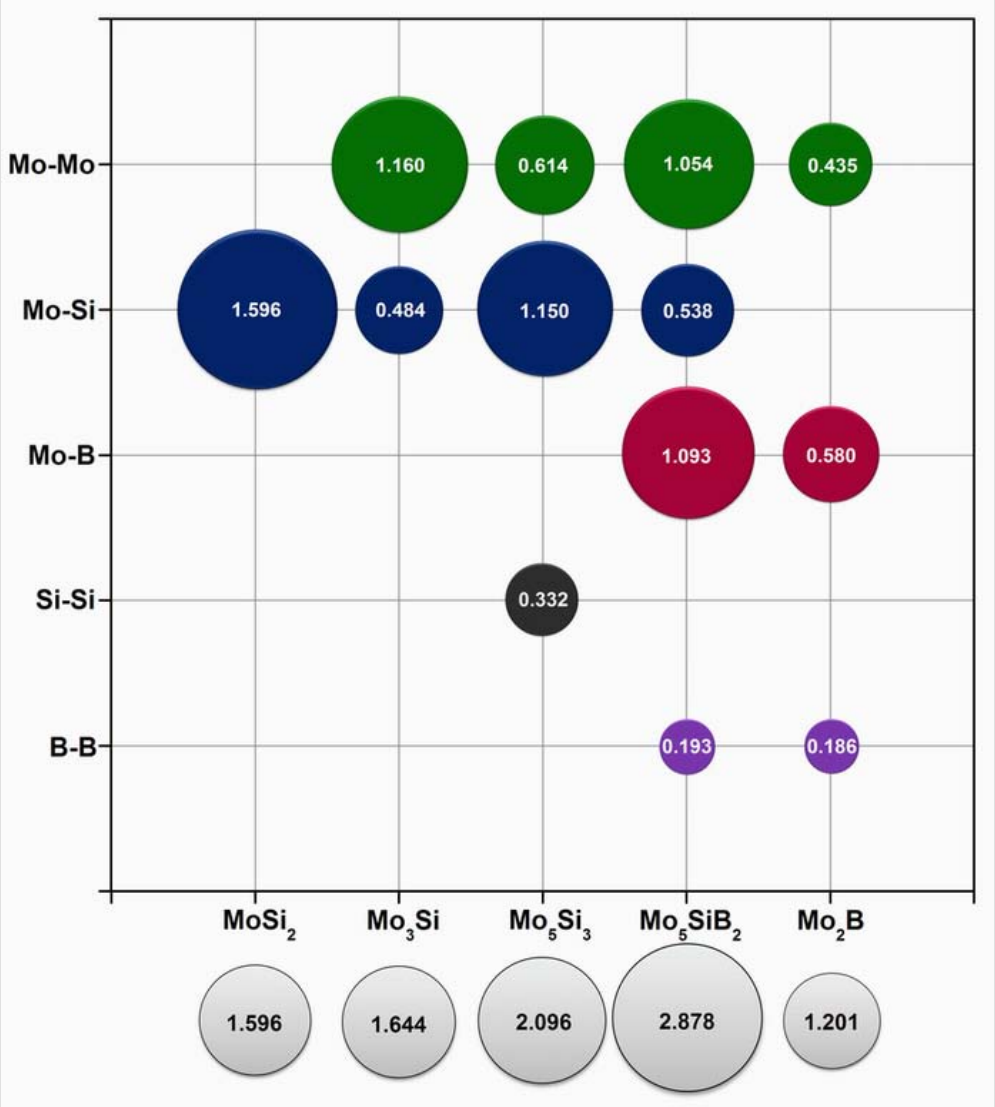
Last year's results: 5 types of bonding in 5 crystals.

Total bond order (BO)(represented by the size of the circles) for five different types of the bonds in the 5 crystals. The total bond order for the crystal is shown at the bottom (x 1/2). Mo_5SiB_2 has the largest circle, or the strongest total bonding.

These and other results suggest that addition of B can enhance the bonding and can significantly improve the alloy properties. We therefore focus our studies on the 2 crystals: Mo_5Si_3 and Mo_5SiB_2.



III. Results for Year 2 (This presentation)

a. Electronic structure and mechanical properties of solid solution models between Mo_5Si_3 and Mo_5SiB_2, effect of B concentration.

$Mo_{160}Si_{64}B_{32}$

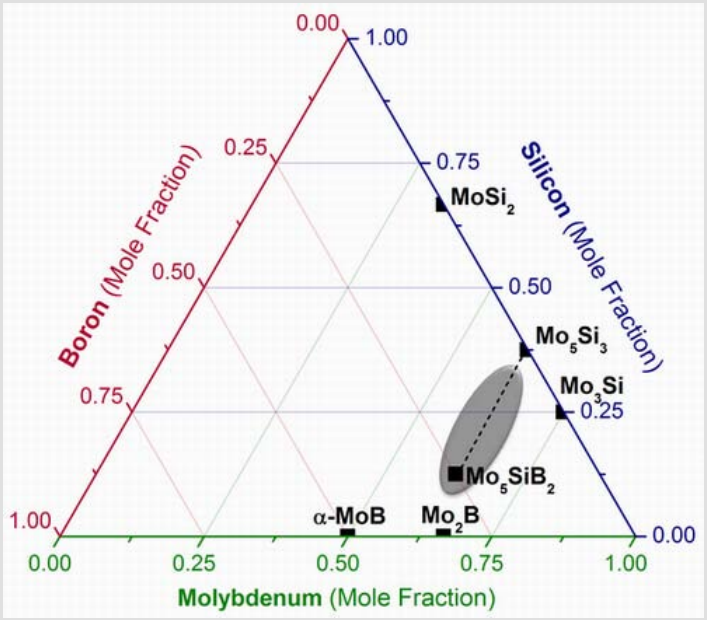
$Mo_{160}Si_{56}B_{40}$

$Mo_{160}Si_{48}B_{48}$

$Mo_{160}Si_{40}B_{56}$

b. Constructing the failure envelopes of Mo_5Si_3 and Mo_5SiB_2.

c. Revised phonon calculations on the five crystals.



Phase diagram within Mo-Si-B system. Four composite models between the two crystalline phases Mo_5Si_3 and Mo_5SiB_2 are studied based on the crystal framework of Mo_5SiB_2.

a. Electronic structure of composite models between Mo_5Si_3 & Mo_5SiB_2

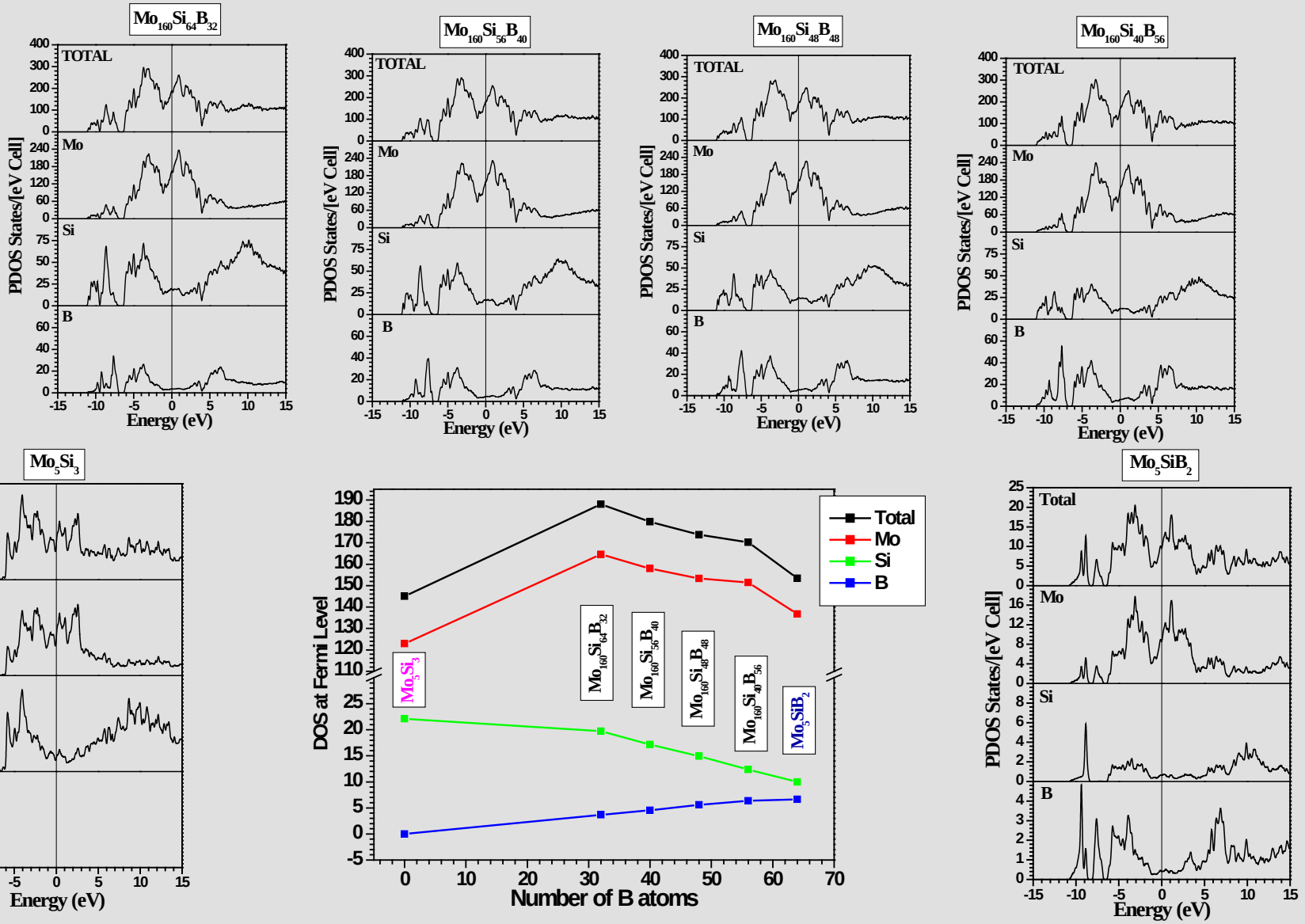


Figure: Calculated total and atom-resolved partial DOS for four composite models and the crystalline Mo_5Si_3 (left) and Mo_5SiB_2 (right). Figure above is the variations of the DOS at $N(E_F)$ for each components.

a. Electronic structure of composite models between Mo_5Si_3 & Mo_5SiB_2

Table 1. Calculated DOS at the Fermi level in the composite models of Mo_5SiB_2 in unit of States/(eV-supercell).

Model	Total	Mo	Si	B
Mo_5Si_3	145.05	122.93 (84.7)	22.12 (15.3%)	-
$Mo_{160}Si_{64}B_{32}$	188.01	164.60 (87.6%)	19.74 (10.5%)	3.68 (1.9%)
$Mo_{160}Si_{56}B_{40}$	179.75	158.02 (87.9%)	17.18 (9.6%)	4.55 (2.5%)
$Mo_{160}Si_{48}B_{48}$	173.81	153.31 (88.2%)	14.92 (8.6%)	5.58 (3.2%)
$Mo_{160}Si_{40}B_{56}$	170.19	151.47 (89.0%)	12.36 (7.3%)	6.36 (3.7%)
Mo_5SiB_2	153.41	136.74 (89.1%)	10.00 (6.5%)	6.66 (4.3%)

Comments on composite models:

1. Both crystalline phases have lower $N(E_F)$ => stability of pure crystalline phases.
2. $N(E_F)$ dominated by states from Mo.
3. For composites with Mo concentration kept the same, Mo $N(E_F)$ varies slightly.
4. $N(E_F)$ components of B and Si do not scale with B concentration.

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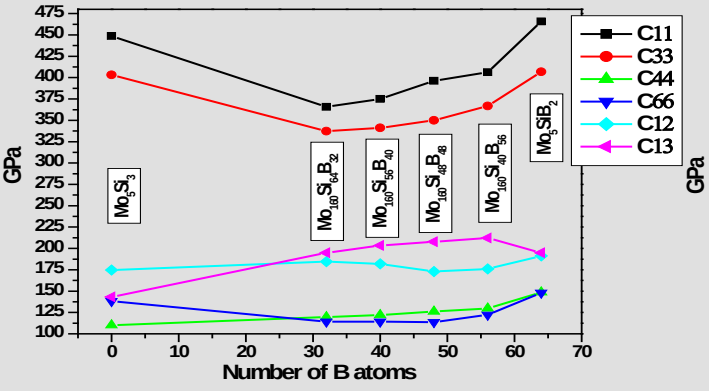
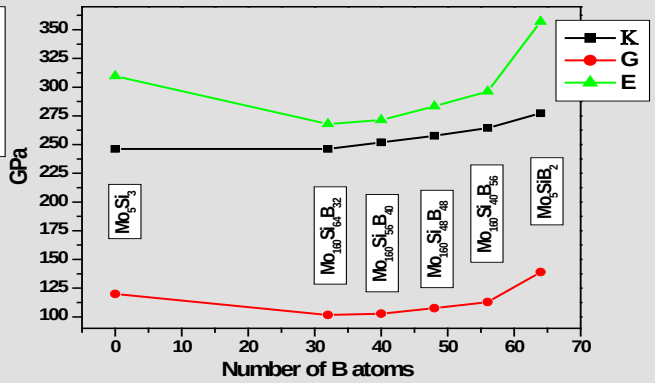
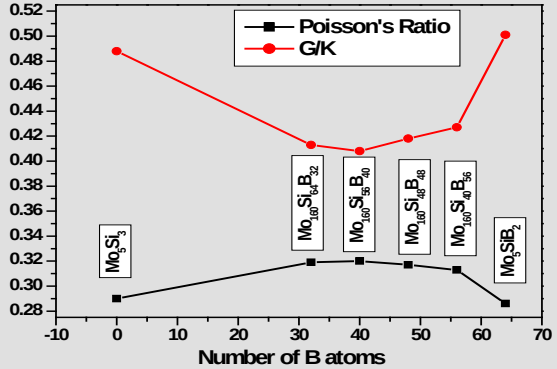
a. Elastic constants & bulk mechanical properties of composite models

Table 2. Calculated elastic constants and bulk properties of supercell composite models $Mo_5(Si_1\text{-}yBy)_3$. Also listed are the models of Mo_5Si_3 (first) and Mo_5SiB_2 (last) (unit in GPa).

Models	C_{11}	C_{33}	C_{13}	C_{12}	C_{44}	C_{66}	K	G	E	η	G/K
$Mo_{160}Si_{96}$	448.8	403.1	143.1	174.7	0.00	138.3	246.9	83.64	225.5	0.348	0.339
$Mo_{160}Si_{64}B_{32}$	365.8	337.3	194.9	184.5	119.7	114.2	246.2	101.6	268.0	0.319	0.413
$Mo_{160}Si_{56}B_{40}$	375.1	341.2	203.3	181.9	122.1	114.3	251.9	102.7	271.3	0.320	0.408
$Mo_{160}Si_{48}B_{48}$	396.2	349.9	207.9	172.8	126.0	113.7	257.6	107.6	283.4	0.317	0.418
$Mo_{160}Si_{40}B_{56}$	406.2	366.7	212.3	176.0	129.8	122.3	264.4	112.8	296.2	0.313	0.427
$Mo_{160}Si_{32}B_{64}$	465.9	406.9	194.8	191.3	148.6	148.2	277.3	138.9	357.0	0.286	0.501







Variations of the mechanical properties as a function of B content

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Observations of above results on composite models

(1) $C_{11} = C_{22}$ in the planer (x-y) directions of the tetragonal cell is larger than C_{33} and they are both much larger than the C_{ij}s in the non-axial directions.

(2) The modulus values of the crystalline phases are always larger than the composites within the current composition range and with the underlining structure of Mo_5SiB_2;

(3) The bulk modulus K, the Young's modulus E and the shear modulus G scale roughly as the B/Si ratio y. The G value is much smaller than E and K in the order of E > K > G.

(4) Individual variations in C_{ij} are related to the direction of applied strain to the model. Only one model for each composition is studied and the symmetry of the crystal is no longer maintained.

(5) The C_{13} values listed are the average of C_{13} and C_{23} and C_{44} is the average of C_{44} and C_{55}. The difference introduced by these approximations should be quite small.

(6) The Pugh ratio G/K for the composite models show small variations but it increased drastically at the end member Mo_5SiB_2 crystal. According to the prevailing theory, a material with G/K < 0.5 is expected to be tough and G/K > 0.5 will be more brittle.

(7) There is a possibility that composite models may be tougher than Mo_5Si_3, but not the Mo_5SiB_2.

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b. Failure envelope in of Mo_5Si_3 and Mo_5SiB_2.

♠ What is failure? How to precisely define failure in terms of mechanical measures of stress, strain or energy is an open question!

♠ In engineering, materials failure is addressed by constructing empirical limit of surfaces in stress or strain spaces. They are used for failure prediction and structure design.

♠ Construction of such surfaces is non-trivial due to difficulty to cover the complete stress-strain spaces experimentally.

♠ Consequently, strength theories have been devised that are considered to be the essential parts of the material constitutive behavior (Mroz 2003).

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b. Failure envelope in of Mo_5Si_3 and Mo_5SiB_2. (continue)

♠ Although, these serve the engineering purpose well, they do not address the fundamental nature of material failure and, in many cases, inadequate for detecting or interpreting failure in laboratory experiments.

♠ Electronic structure and bonding are at the heart of material strength and stiffness. Therefore, we have to explore the failure process through 'theoretical' experiments using *ab initio* simulations on crystals.

♠ We propose a method to construct the failure envelope of a crystal using data from multi-axial tensile experiment.

♠ This is an example of multi-scale modeling connecting microscale and macroscale properties.

Procedures to construct failure envelop using multi-axial data

♠ The strength of a material is characterized by a 3-d failure envelope (surface of failure points) in the stress space (σ_{xx}, σ_{yy}, σ_{zz}).

♠ The "experiments" are performed on a supercell by applying successive tensile strains (ε_{xx}, ε_{yy}, ε_{zz}) in small steps until the stress reaches the failure point.

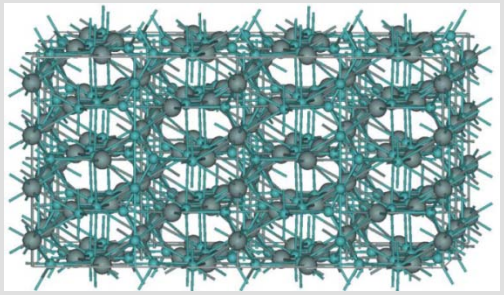
♠ The "experiment" is carried out in as many directions (multi-axial) as feasible.

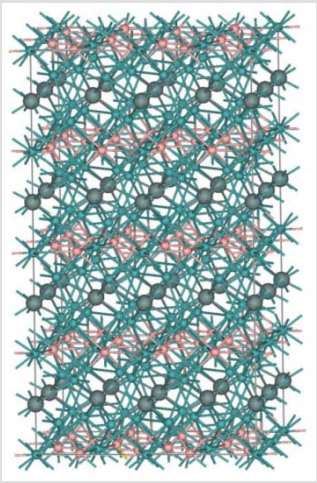
♠ The final set of stress data (σ_{xx}, σ_{yy}, σ_{zz}) at the failure points are used to construct a failure envelop in the 1st quadrant of the σ space.

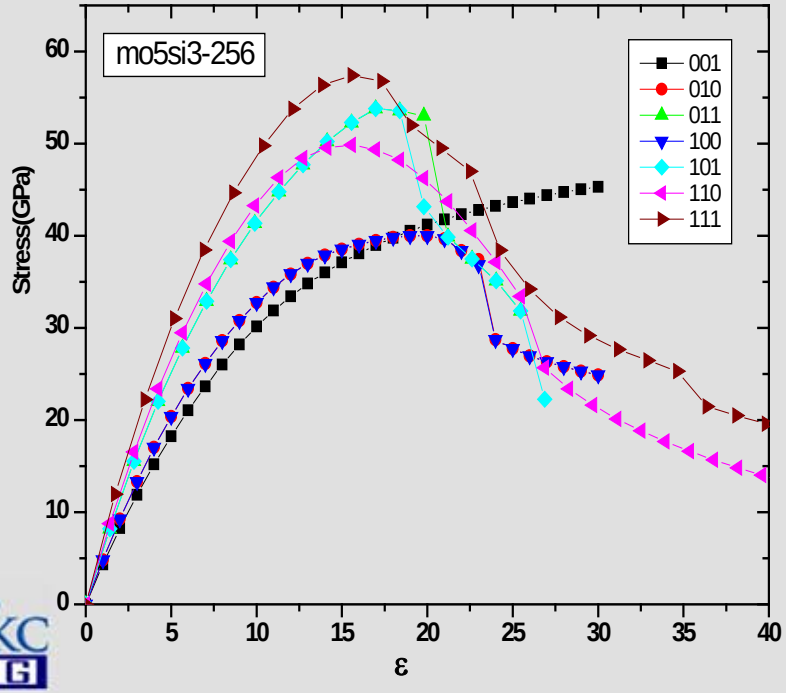
♠ The total area (or volume enclosed) of the envelope constitutes a single parameter representing the average strength of a materials under tensile deformation.

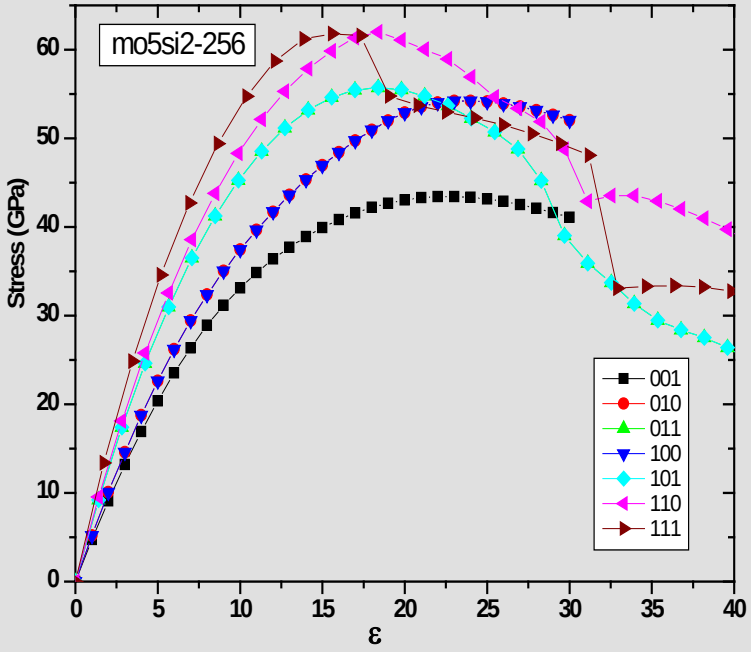
♠ The shape and color of the envelope delineate the variations of the strength in different directions.

Stress vs. strain curves on supercells (256 atoms) of Mo_5Si_3 and Mo_5SiB_2 along 7 principal directions. The failure point is defined as the strain with the maximum stress in the curve for a given direction.









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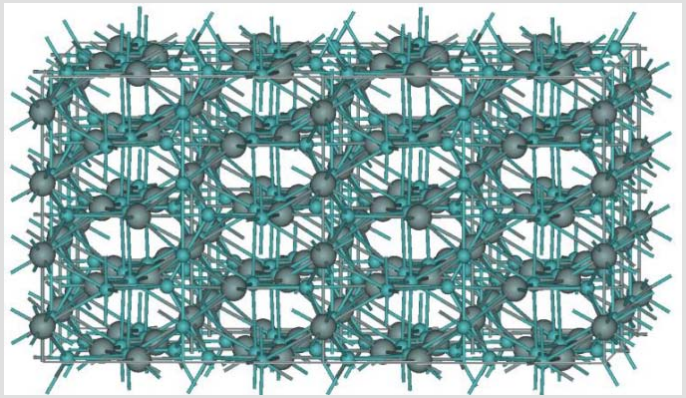
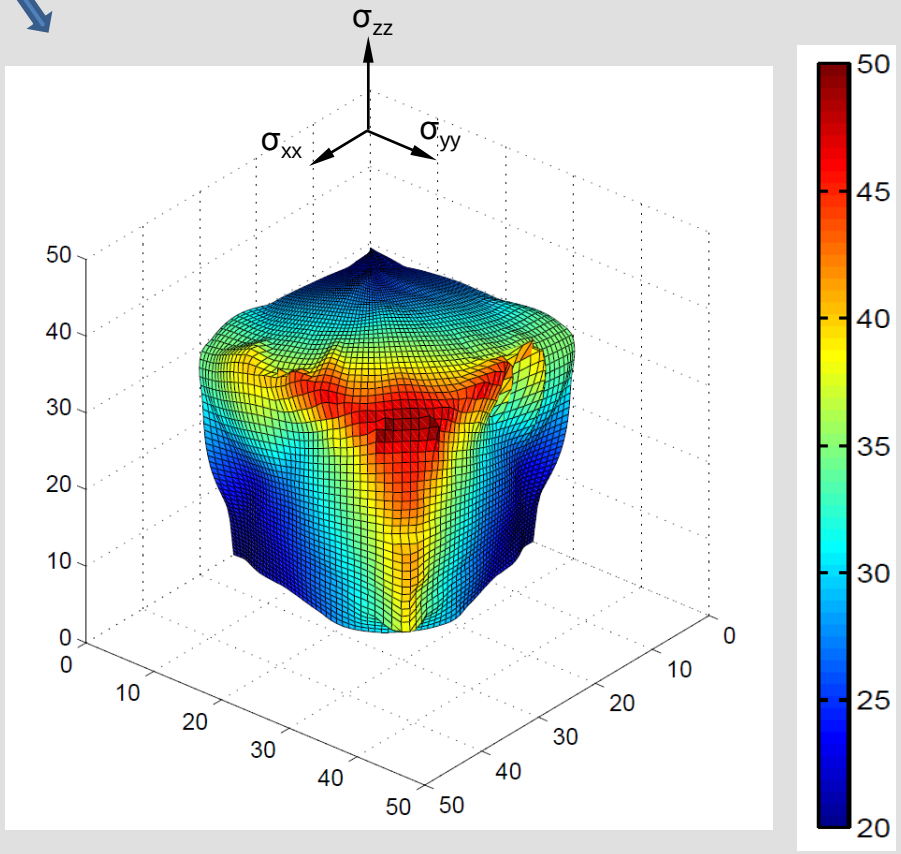
Multi-axial failure envelope in Mo_5Si_3 (237 data points)

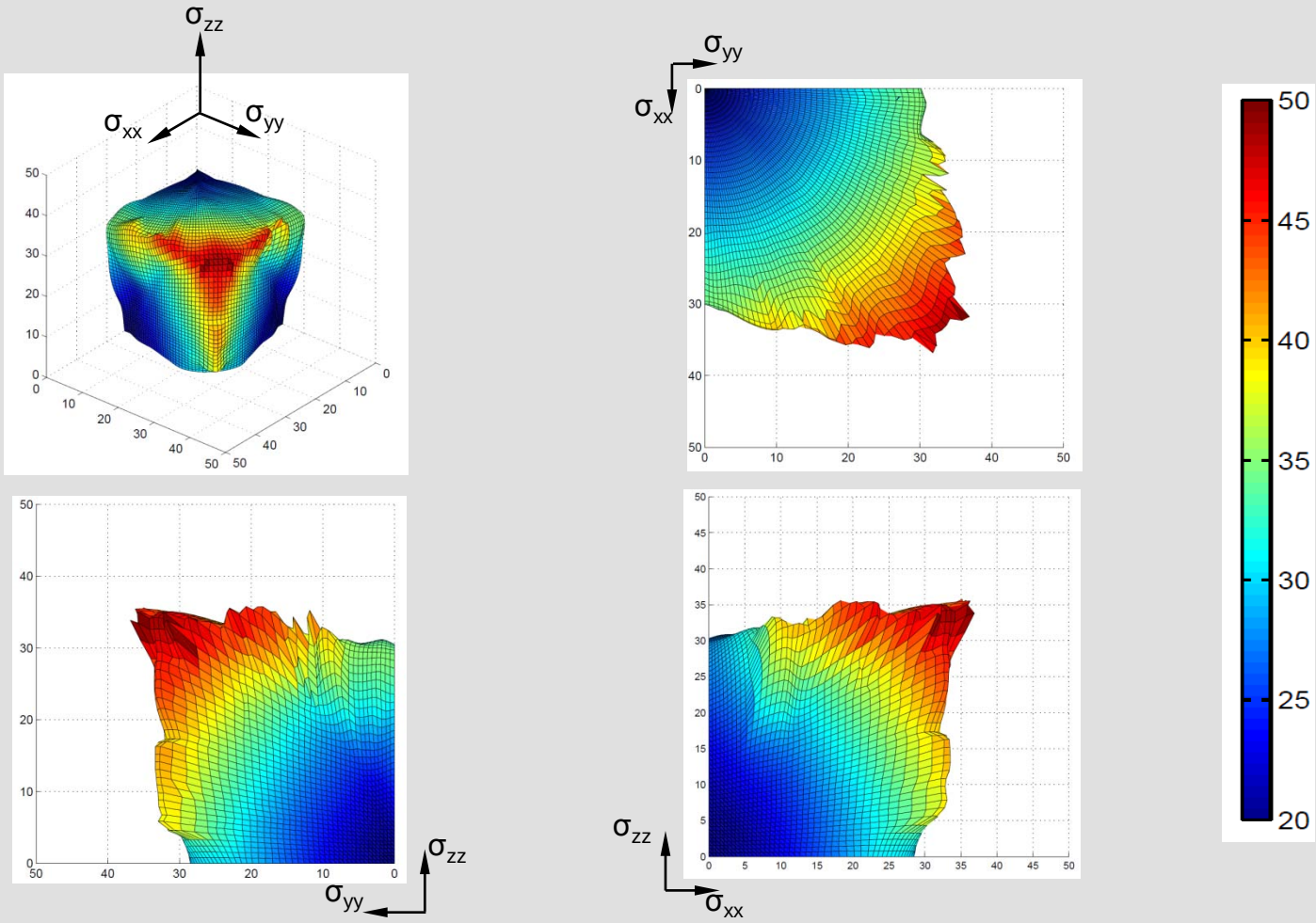


Orthorhombic 256-atom supercell model of Mo_5Si_3 used for tensile experiment for failure envelope.



♠ Total volume enclosed: $2.800 \times 10^4 (Å)^3$;
Total surface area: $2.157 \times 10^3 (Å)^2$.

Failure envelope of Mo_5Si_3 (viewed in 3 directions)

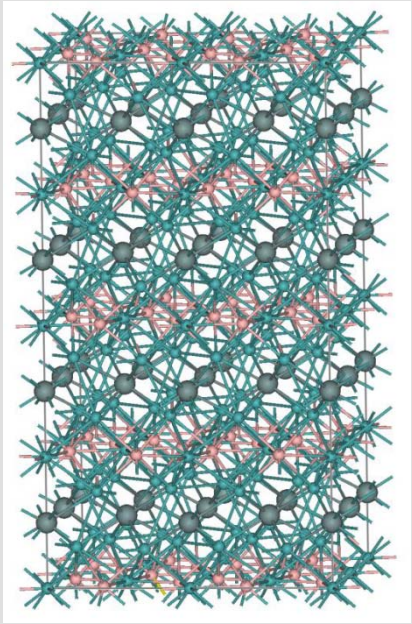


Observations:

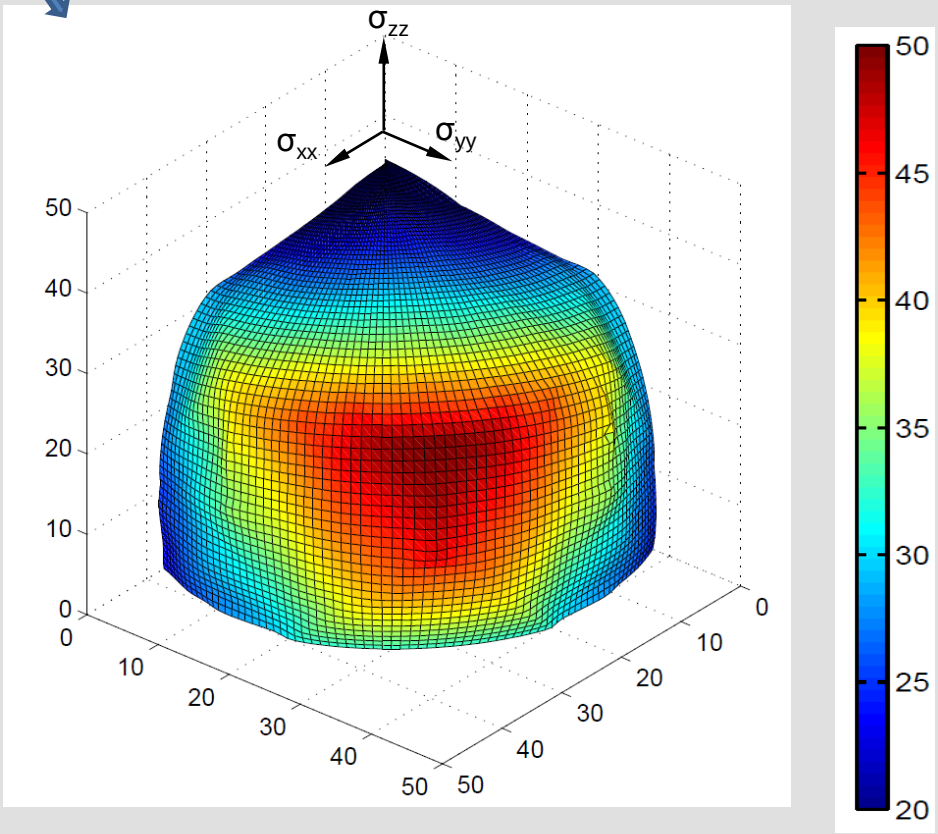
♠ Strong anisotropy, very strong in the (111) direction.

♠ Surface quite rough.

Multi-axial failure envelope of Mo_5SiB_2 (239 data points)



Orthorhombic 256-atom supercell model of Mo_5SiB_2 used for tensile experiment for failure envelope.



♠ Total volume enclosed: $5.473 \times 10^4 (Å)^3$; (95.5% **larger** than in Mo_5Si_3).
Total surface area: $3.424\ 10^3 (Å)^2$; (58.7% **larger** than in Mo_5Si_3).

♠ Mo_5SiB_2 is much stronger than Mo_5Si_3 based on failure envelope analysis.

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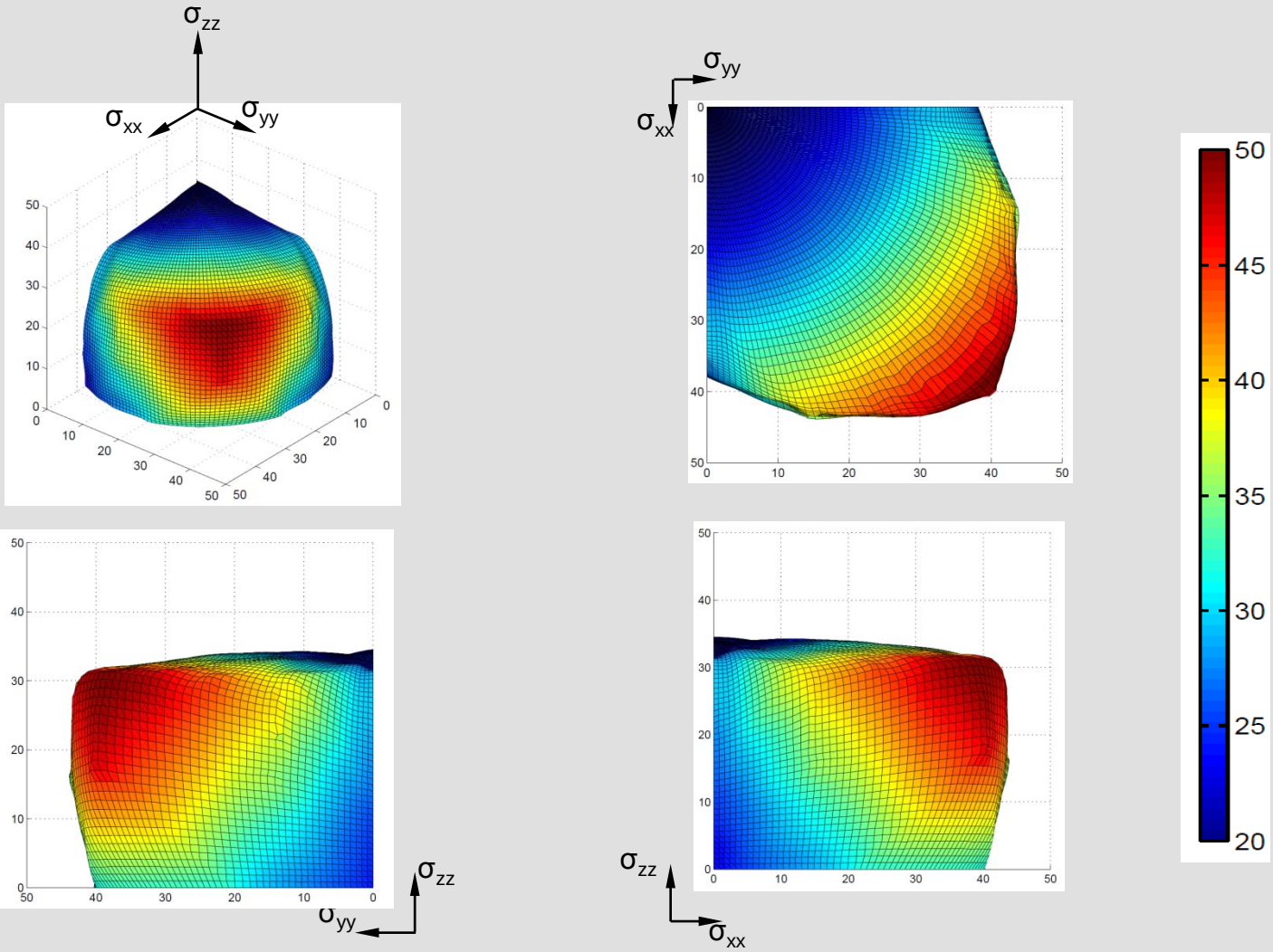
Failure envelop of Mo_5SiB_2



Observations:

♠ Strong direction is still (111), less anisotropy. Surface relatively smooth.

♠ Shape, size and location of red areas different from Mo_5Si_3.

c. Revised phonon calculations on 5 crystals

I. Importance of phonon calculation in high temperature studies.

II. Importance of phone spectra to experimental data interpretation.

III. Why revise? Previous calculation using smaller number of k points in the cell which may affect the accuracy.

IV. Revised calculation using a larger number of k points and corrected the labeling.

V. In Mo_5Si_3, the changes are very large due to an error in the previous calculation. In other 4 crystals, the changes are other relatively small.

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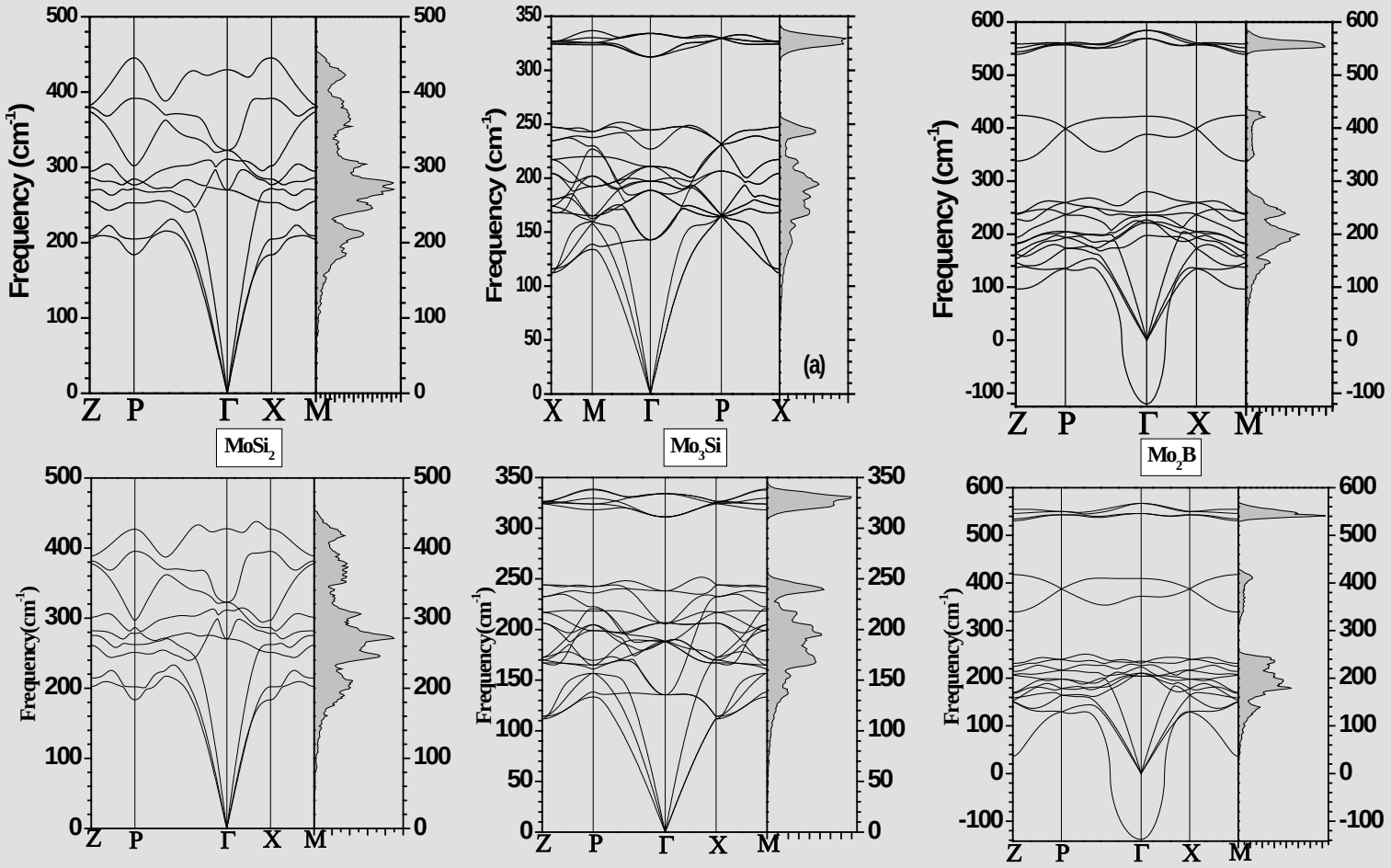
Comparison between previous calculations (upper) and revised calculation (lower) for $MoSi_2$, Mo_3Si, Mo_2B.



Observations:

♠ Note the difference in the maximum frequency. Higher modes correspond to lighter atoms. Lower modes are from heavier Mo atoms.

♠ Mo_2B has a negative mode at Gamma => lattice instability at finite temperature.

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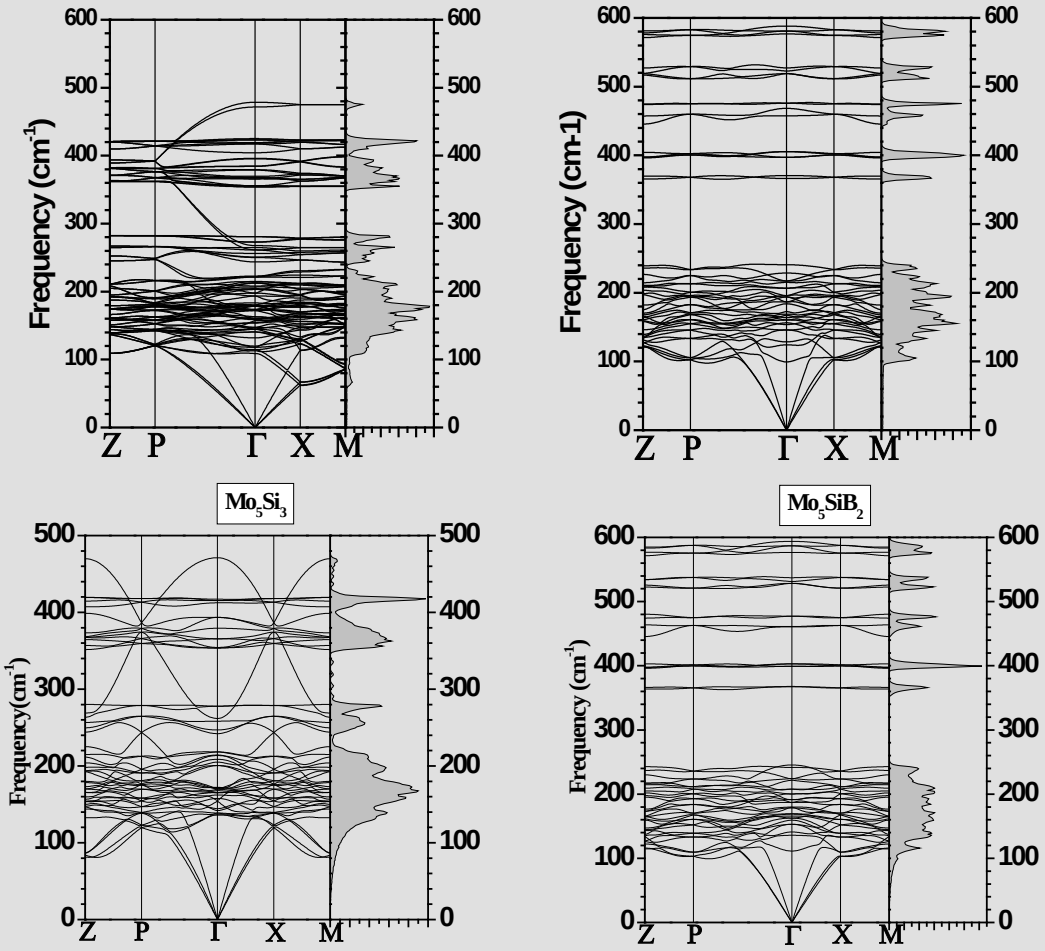
Comparison between previous calculations (upper) and revised calculation (lower) Mo_5Si_3, and Mo_5SiB_2.



Observations:

♠ The difference in Mo_5SiB_2 is minimal.

♠ The difference in Mo_5Si_3 is substantial because of an error in the lattice constant specification.

♠ Mo_5SiB_2 has many vibrational modes at frequencies between 500-600 cm^{-1} related to the vibration of the B atoms.

♠ The phonon frequencies $\hbar\omega_j$ will be used for vibrational free energy calculation.

IV. Conclusions for the work in the second year

♠ The second year consists mostly of many tasks for the 2nd mile stone. Significant results have been obtained.

♠ The study of the electronic structure and elastic properties of the composite models between Mo_5Si_3 and Mo_5SiB_2 has been started with some results obtained and additional calculations are on the way.

♠ A new initiative in the construction of failure envelope in Mo-based compounds was initiated and applied to supercells of Mo_5Si_3 and Mo_5SiB_2 by executing uniaxial tensile experiments. Clear evidence of the superior mechanical properties of Mo_5SiB_2.

♠ The phonon calculation for the five crystals were repeated with increased accuracy. The results indicate the importance of using sufficient number of k-points to obtain more accurate results.

♠ Computational tools and programs were developed in the course of carrying out the above tasks.

V. Plan for the next year

In the third year (final year), our plan is in accordance with SOPO.

1. Method and code development focusing on the temperature dependent properties.
2. Use both classical and *ab initio* molecular dynamic simulations for Mo_5Si_3 and Mo_5SiB_2 crystals for temperature up to 1800K.
3. Snapshots of the structures at elevated temperature will be further refined and used to evaluate the mechanical properties.
4. Additional simulation on composite models using the underling crystal structure of Mo_5Si_3.
5. Work on the analysis of failure envelope will continue.
6. Substitution of Mo by Nb or Cr to improve the overall alloy properties will be explored.

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VI. Review of milestones and time line

There are four milestones to be reached within 3 years for this project based on the tasks and subtasks outlined in SOPO.

[1] Mechanical properties and electronic structure of the 5 crystalline phases in the Mo-Si-B system.

Milestone date: to be finished in first year.

Status as of June 2011: **milestone reached!**

[2] Development of the new computational method. Test of the computational codes on simple crystals.

Milestone date: to be completed by the end of second year.

Status as of June 2012: new method development in excellent progress, results reported in this presentation! **Milestone reached!**

[3] Supercell modeling of composite alloys and identification of those with promising properties.

Milestone date: to be completed by the end of second year.

Status as of June 2012: Composite alloys work started with substantial results reported in this presentation. **Milestone will be reached.**

[4] Application of the new method to supercell models of composite alloys and exploration of new materials.

Milestone date: Targeted for completion by the end of the third year.

Status as of June 2012: Projects will start soon and milestone expect to be reached by the end of the third year.

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THANK YOU !

WE GREATLY APPRECIATE DOE-NETL SUPPORT!

PROGRAM MANAGER: DR. RICHARD DUNST